

EXHIBIT A



Attorney's Docket No.: 15313.0002

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the application of: McEwan et al.
Serial No.: 10/520,369
Filed: June 15, 2005
For: *Method of chemical ionization mass spectrometry*

Examiner: Weisz, David G
Group Art Unit: 4153

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DECLARATION OF MURRAY J. MCEWAN UNDER 37 C.F.R. §1.132

I, Murray J. McEwan, declare:

1. I am the co-inventor of the subject matter described and claimed in the above-captioned patent application.
2. I have reviewed the Office Action mailed June 23, 2009 ("Office Action") issued in the above-mentioned application. In this Office Action, claims 1-6 were rejected under 35 U.S.C. § 103(a) as being obvious over Freitas et al. (*Int J Mass Spectrom.*, Vol. 175, p. 107-122 (1998)) ("Freitas"). I have reviewed the Freitas reference listed above.
3. The Freitas reference used a modified flowing afterglow (FA) apparatus. There are some problems with this FA technique in that all ions produced in the discharge can react with an added reactant molecule and it can be difficult to decide which product ion arises from which reactant molecule. It was this problem that led to the adaption of the SIFT method for monitoring ion-molecule reactions (D Smith, NG Adams. *In recent Advances in Flow Tubes: Gas phase Ion Chemistry*, 1979, Academic Press, p. 1-44) which essentially led to the demise of the FA technique.
4. The flowing afterglow selected ion flow tube technique (FA-SIFT) is recognized as the most effective technique for monitoring reactions of ion molecule reactions at thermal energies (D Smith, NG Adams. *The Selected Ion Flow tube: Studies of ion-neutral reactions*, *In Advances in Atomic and Molecular Physics*. 1988, V24, Academic Press, p. 1-49). In a modified version this is also called the SIFT technique.

5. In the paragraphs below, I will compare the data produced in two papers: (1) PF Wilson, MJ McEwan and M Meot-Ner, *Int J Mass Spectrom. Ion Proc.*, 1994, Vol. 132, p. 149-

152 (attached at Appendix A) and (2) PF Wilson, DB Milligan, LW Lam, CG Freeman, M Meot-Ner and MJ McEwan. *J Amer Soc. Mass Spec.*, 2002, Vol. 13, p.1028-1033 (attached at Appendix B), using the preferred FA-SIFT technique with that of the Freitas reference using their flowing afterglow method and demonstrate some of the problems with method described in Freitas reference. Persons skilled in the art would choose SIFT results over flowing afterglow where there is conflict.

6. One of the first papers on the reactions of the methoxymethyl cation using SIFT was published by our group, Wilson et al in 1994 (*Int J Mass Spectrom. Ion Proc.*, 1994, 132, 149-152). In that paper we examined the reactions of $\text{CH}_3\text{COCH}_2^+$ with nitrogen bases and achieved reasonable overlap in compounds (but not results) studied in Freitas reference as the Freitas reference also published results from several nitrogen bases. The second paper was also a paper from our group, Wilson et al, *Mass Spec.*, 2002, Vol. 13, p. 1028-1033 ("Wilson"), in which we measured the reactions of nitrogen bases as well as sulfur compounds and hydrocarbons. In that Wilson reference, we showed that quite a number of the rate coefficients published by Freitas reference were incorrect (see Table 1 of Wilson).

7. The Freitas reference claims a rapid reaction of $\text{CH}_3\text{OCH}_2^+$ and H_2S (Table 2 of Freitas) while the Wilson reference shows there is in fact no reaction ($k < 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$). That represents an error of 4 orders of magnitude. A glance at Table 1 in Wilson shows that for most reactions where overlap occurs between Wilson and Freitas references, the Freitas reference results are in error by around a factor of 2.

8. The only hydrocarbon reactant that the Freitas reference measured with $\text{CH}_3\text{OCH}_2^+$ was C_6H_6 and a fast reaction was reported ($1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$). The Wilson reference reported a much slower reaction ($4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and showed that there was no reaction of $\text{CH}_3\text{OCH}_2^+$ with small straight chain hydrocarbons but fast reactions occurred with odorant hydrocarbons CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, $(\text{CH}_3)_2\text{SH}$. With findings based on the Freitas reference alone, it would be reasonable to assume that reactions of $\text{CH}_3\text{OCH}_2^+$ occur with hydrocarbons.

9. Accordingly, the Freitas reference does not teach or suggest a method of detecting and quantifying a gas sample containing trace levels of molecules containing one or more of a range of reactive species in gases or gas mixtures containing alkanes, ethene, or ethyne in a selected ion flow tube mass spectrometer wherein the alkoxyxymethyl cations do not react with the major components of air, nor with the gas or the gas mixtures containing alkanes, ethene or

Applicant : McEwan et al.
Serial No. : 10/520,369
Filed : June 15, 2005
Page : 3 of 3

Attorney's Docket No.: 15313.0002

ethyne but reacts with the trace levels of molecules to be detected as described in claims 1 and 4.
There is also no motivation or suggestion in the Freitas reference to modify the methods described in the above-cited references to arrive at the method described in claims 1 or 4.

10. All statements made herein of my knowledge are true and all statements made on information and belief are believed to be true; and further these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patents issued thereon.

Date: 19 Dec 2009

M. J. McEwan
Murray J. McEwan

Witnessed by: Jane

JANE ELIZABETH PAIRMAN
BARRISTER & SOLICITOR
CHRISTCHURCH

APPENDIX A

Short Communication

Reactions of $\text{CH}_3\text{OCH}_2^+$ with nitrogen bases: a mechanism for the formation of protonated imines

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(Received 24 May 1993; accepted 18 October 1993)

Abstract

The $\text{CH}_3\text{OCH}_2^+$ ion reacts with NH_3 and with primary and secondary amines R_2NH with the elimination of CH_3OH to form the protonated imines R_2NCH_2^+ . Proton transfer and methyl cation transfer, although exothermic, are not major channels. Elimination of CH_3OH is also observed with $\text{C}_2\text{H}_5\text{OH}$ to form $\text{C}_2\text{H}_5\text{OCH}_2^+$. No reaction is observed with HCN , while methyl cation transfer to form $\text{CH}_3\text{CNCH}_2^+$ is the main channel with CH_3CN . The reactivity of the CH_3CHOH^+ isomer is different, with fast proton transfer to CH_3CN and NH_3 . With CH_3CN , a fast three-body association channel is also observed.

Key words: $\text{CH}_3\text{OCH}_2^+$; Nitrogen bases; Protonated imines

Introduction

The $\text{CH}_3\text{OCH}_2^+$ ion can be formed by several ion/molecule mechanisms. Its formation and reactions may be of interest in the interstellar environment, in clouds such as OMC-1 in the Orion–Monoceros complex, where CH_3OH is abundant [1]. In such environments the reaction of CH_3OH_2^+ with the common interstellar species H_2CO can form the $\text{CH}_3\text{OCH}_2^+$ ion [2]. The ion can also form as a fragment of CH_3OCH_3 , which is also present in these clouds. In this paper we report the reactions of $\text{CH}_3\text{OCH}_2^+$ with NH_3 and other bases, including some that are abundant in several regions of interstellar clouds.

Experimental

The experiments were performed on the selected ion flow tube (SIFT) apparatus of the University of

Canterbury [3]. The reactions were studied in a He carrier gas at a total pressure of 0.4 mbar at (295 ± 10) K. The reactant ions were generated in the ion source by electron impact on dimethoxy-methane $\text{H}_2\text{C}(\text{OCH}_3)_2$. Small flows of the reactant neutrals were added at the downstream inlet port and the decay of the $\text{CH}_3\text{OCH}_2^+$ ion signal with reactant flow was measured in the usual way.

The injection of $\text{CH}_3\text{OCH}_2^+$ into the flow tube was accompanied by partial fragmentation up to about 40% of the total ion population, with HCO^+ and CH_3^+ being the fragment ions produced. Both of these fragment ions may then undergo proton transfer with the neutral reagent. HCO^+ readily transfers a proton to species with higher proton affinity than CO. The (about 15%) CH_3^+ fragment can also transfer a proton to NH_3 [4] and to $(\text{CH}_3)_2\text{NH}$ as Table 1 shows, and presumably to other amines as well. The fragmentation could not be avoided under any conditions of injection that produced sufficient $\text{CH}_3\text{OCH}_2^+$ signal.

Because of the fragmentation during the

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Table 1
Rate coefficients for the reactions of $\text{CH}_3\text{OCH}_2^+$, CH_3CHOH^+ and CH_3^+ with neutrals B

B	Major products	k ^a	ΔH° ^b	$\Delta H^\circ(\text{PT})^c$	$\Delta H^\circ(\text{MCT})^d$	Method
<i>Reactions of $\text{CH}_3\text{OCH}_2^+$</i>						
HCN		< 0.01	220.3	102.3	-40.8	SIFT
HCOOH	products	0.29		72.2	-0.9	SIFT
CH_3OH	$\text{CH}_3\text{OCH}_2^+ \cdot \text{CH}_3\text{OH}$	0.013	0	59.0	-22.1	SIFT
CH_3CN	$\text{CH}_3\text{CNCH}_2^+ + \text{H}_2\text{CO}$	0.31		33.4	-74.7	SIFT
	$\text{CH}_3\text{OCH}_2^+ \cdot \text{CH}_3\text{CN}$	0.02				SIFT
NH ₃	$\text{CH}_3\text{NH}_2^+ + \text{CH}_3\text{OH}$	0.43 ^e	-67.4	-33.7	-108.8	ICR
		0.59 ^e				SIFT
CH_3NH_2	$\text{CH}_3\text{NHCH}_2^+ + \text{CH}_3\text{OH}$	0.94	-140.6	-75.6	-154.7	ICR
		1.5				SIFT
$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_2\text{H}_5\text{NHCH}_2^+ + \text{CH}_3\text{OH}$	1.4	-158.1	-88.1	-166.2	ICR
		1.5				SIFT
$(\text{CH}_3)_2\text{NH}$	$(\text{CH}_3)_2\text{NCH}_2^+ + \text{CH}_3\text{OH}$	0.37	-179.1	-103.1	-183.2	SIFT
$(\text{CH}_3)_3\text{N}$	$\text{CH}_3\text{OCH}_2^+ \cdot (\text{CH}_3)_3\text{N}$	1.4		-121.9	-202.0	SIFT
<i>Reactions of CH_3CHOH^+</i>						
CH_3CN	$\text{CH}_3\text{CNH}_2^+ + \text{CH}_3\text{CHOH}$	3.0		-7.0		ICR
	$\text{CH}_3\text{CNH}_2^+ \cdot \text{CH}_3\text{CHOH}$	0.2				ICR
NH ₃	NH ₄ ⁺	1.8		-72.5		ICR
<i>Reactions of CH_3^+</i>						
CH_3OCH_3	$\text{CH}_3\text{OCH}_2^+ + \text{CH}_4$	0.35	-326.8			SIFT
$(\text{CH}_3)_2\text{NH}$	$(\text{CH}_3)_2\text{NH}_2^+ + \text{CH}_2$	2.1	-876.8			SIFT

^a In units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$. Error estimate $\pm 20\%$. The rate coefficient is for the overall reaction of $\text{CH}_3\text{OCH}_2^+$ with B to form the major product as shown.

^b Enthalpy change to yield the major products as shown. Thermochemical data from Ref. 5.

^c Enthalpy change of proton transfer $\text{CH}_3\text{OCH}_2^+ + \text{B} \rightarrow \text{BH}^+ + c\text{-CH}_2\text{CH}_2\text{O}$, thermochemical data from Ref. 5. The possible proton transfer channel is absent with NH₃, CH₃NH₂ and C₂H₅NH₂, and less than 50% with (CH₃)₂NH and (CH₃)₃N.

^d Enthalpy change of methyl cation transfer. Thermochemical data from Ref. 5. For $\text{CH}_3\text{CNCH}_2^+$, we use $\Delta H_f^\circ = 424 \text{ kJ mol}^{-1}$, Ref. 8, and for $(\text{CH}_3)_4\text{N}^+$, we use $\Delta H_f^\circ = 540 \text{ kJ mol}^{-1}$, estimated from the NH₄⁺, CH₃NH₂⁺, (CH₃)₂NH₂⁺ and (CH₃)₃NH⁺ series. If the methyl cation transfer channel does occur, it is less than 15% of the total reaction.

^e Compare with $0.13 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$ in Ref. 6(d).

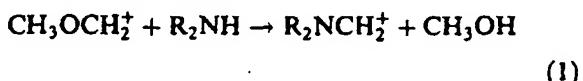
injection process, accurate product distributions, i.e., comparison of channel (1) and (2) below vs. possible proton transfer, could not be achieved. For this reason, we also performed ion cyclotron resonance (ICR) using the ICR apparatus at the Jet Propulsion Laboratory, on several of the reaction systems. In these experiments, $\text{CH}_3\text{OCH}_2^+$ was generated by electron impact on CH_3OCH_3 . The rate coefficients obtained by SIFT and ICR were in very good agreement for NH₃ and C₂H₅NH₂, and in reasonable agreement for CH₃NH₂. We also performed several ICR measurements on the reactions of the CH_3CHOH^+ isomer, obtained by self-protonation of CH₃CHO, in mixtures of 5:1 CH₃CHO with CH₃CN or NH₃, at total pressures of 10^{-7} to 10^{-5} mbar, at a nominal temperature of 298 K.

Results and discussion

Elimination of CH_3OH and the formation of protonated imines

The reactions studied, their rate coefficients and thermochemistry are summarized in Table 1.

With alcohols and amines, $\text{CH}_3\text{OCH}_2^+$ reacts with the elimination of CH_3OH as the main channel, as in reactions (1) and (2), which are exothermic [5]. Reaction (1) with C₂H₅NH₂ and (C₂H₅)₂NH [6b] and with NH₃ and vibrationally excited $\text{CH}_3\text{OCH}_2^+$ were observed [6c,d]:



With HCOOH, which has an acidic hydrogen, $\text{CH}_3\text{OCH}_2^+$ reacts rapidly, but the reaction analogous to reaction (1) is not observed, possibly because other alternative channels are available. No CH_3OH elimination is observed with reactants that have only alkyl protons.

The most likely mechanism for reaction (1) is attack by the $-\text{CH}_2^+$ carbon on the N center, followed by proton shift from CH_2^+ , or from the NH groups of the neutral. The source of the proton was determined by deuterium labelling as the ND_3 molecule in the $\text{CH}_3\text{OCH}_2^+ + \text{ND}_3$ system [6c,d].

Alternative channels

The formation of NH_4^+ and $\text{CH}_3^+\text{NH}_3^+$ in $\text{CH}_3\text{OCH}_2^+ + \text{NH}_3$ was reported in non-thermal systems and in a complex reaction system containing other electron impact products of CH_3OCH_3 , which may also protonate NH_3 [6]. However, proton transfer is not observed and the formation of CH_3NH_3^+ was a minor channel in the present ICR experiments in Table 1. Similarly, in the SIFT experiments with $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$, although this proton transfer cannot be ruled out because of the reactions of the HCO^+ fragment, it is at most minor channel, less than 50%, and in fact we have no evidence for its occurrence at all.

Although proton transfer to produce CH_3CHO or CH_2CHOH would be exothermic with most of the reactants, it would require substantial rearrangement [5]. For example, this channel does not occur with CH_3OH and CH_3CN . In reactions of $\text{CH}_3\text{OCH}_2^+$ with CH_3OH and CH_3CN , proton transfer with rearrangement to form the CH_3CHO neutral would be exothermic by 54.2 and 79.8 kJ mol^{-1} respectively, and with rearrangement to form CH_2CHOH , by 13.4 and 39.0 kJ mol^{-1} , respectively.

Proton transfer to form c- $\text{CH}_2\text{CH}_2\text{O}$ possibly through a CH_2OCH_2 intermediate does not require major rearrangement, but it is endothermic with the oxygen bases in Table 1. The reaction with the amines would be exothermic, but is not observed, as noted above. Evidently the more exothermic reaction (1) is preferred.

No significant methyl cation transfer channel is observed in the present reaction systems, except with CH_3CN , although this is the most exothermic channel with all the reactants, as seen in Table 1. No reaction is seen between $\text{CH}_3\text{OCH}_2^+$ and HCN , and only a slow association reaction is seen with CH_3OH , although a slow methyl cation transfer reaction with the latter was observed at low pressures [2]. The lack of reaction may be ascribed to the small exothermicity, combined with an energy barrier that is known in methyl cation transfer reactions [7].

In this respect, it is interesting to compare the reactivity of $\text{CH}_3\text{OCH}_2^+$ with that of CH_3OH_2^+ . The latter ion does transfer a methyl cation to alcohols, although at slow rates [2]. The only observed methyl cation transfer in the present study was to CH_3CN , where this channel is significantly exothermic, while the other channels are endothermic. However, no reaction was observed with HCN , where methyl cation transfer would be somewhat less exothermic. These observations with CH_3CN and HCN indicate a fairly strong sensitivity of the reaction rate to exothermicity, or to the presence of other controlling factors such as possible energy barriers. The reaction with CH_3CN suggests similar reactions with other alkynitriles.

With the amines, reaction (1) is preferred to the more exothermic methyl cation transfer. Again, a possible reason may be the presence of energy barriers to methyl cation transfer [7], and an absence of such barriers to the fast reaction (2).

In the reaction of $\text{CH}_3\text{OCH}_2^+$ with $(\text{CH}_3)_3\text{N}$, proton transfer leading to c- $\text{CH}_2\text{CH}_2\text{O}$ would be exothermic by 122 kJ mol^{-1} , and methyl cation transfer by 202 kJ mol^{-1} . Under SIFT conditions, neither channel is observed, and a fast reaction leads to the formation of the adduct.

Reactions of CH_3CHOH^+ and CH_3^+

Reaction (1) is useful in distinguishing between $\text{CH}_3\text{OCH}_2^+$ and its more stable isomer, the CH_3CHOH^+ ion. We observed that CH_3CHOH^+

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^b Enthalpy change to yield the major products as shown. Thermochemical data from Ref. 5.

^c Enthalpy change of proton transfer $\text{CH}_3\text{OCH}_2^+ + \text{B} \rightarrow \text{BH}^+ + \text{c-CH}_2\text{CH}_2\text{O}$, thermochemical data from Ref. 5. The possible proton transfer channel is absent with NH_3 , CH_3NH_2 and $\text{C}_2\text{H}_5\text{NH}_2$, and less than 50% with $(\text{CH}_3)_2\text{NH}$ and $(\text{CH}_3)_3\text{N}$.

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^e Compare with $0.13 \times 10^{-9} \text{ cm}^3 \text{s}^{-1}$ in Ref. 6(d).

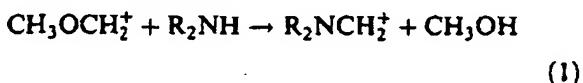
injection process, accurate product distributions, i.e., comparison of channel (1) and (2) below vs. possible proton transfer, could not be achieved. For this reason, we also performed ion cyclotron resonance (ICR) using the ICR apparatus at the Jet Propulsion Laboratory, on several of the reaction systems. In these experiments, $\text{CH}_3\text{OCH}_2^+$ was generated by electron impact on CH_3OCH_3 . The rate coefficients obtained by SIFT and ICR were in very good agreement for NH_3 and $\text{C}_2\text{H}_5\text{NH}_2$, and in reasonable agreement for CH_3NH_2 . We also performed several ICR measurements on the reactions of the CH_3CHOH^+ isomer, obtained by self-protonation of CH_3CHO , in mixtures of 5:1 CH_3CHO with CH_3CN or NH_3 , at total pressures of 10^{-7} to 10^{-5} mbar , at a nominal temperature of 298 K.

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reacts with CH_3CN and NH_3 , through fast proton transfer, as shown in Table 1. Interestingly, with CH_3CN adduct formation was also observed, apparently in a three-body reaction with a rate coefficient $> 5 \times 10^{-26} \text{ cm}^6 \text{s}^{-1}$. This is several orders of magnitude faster than many three-body clustering reactions, and joins a group of association reactions where the association complex lasts sufficiently long for stabilization on the time-scale of the ICR experiment [9,10].

In relation to interstellar reactions, $\text{CH}_3\text{OCH}_2^+$ can be formed by the reaction of CH_3OH_2^+ with CH_2O [2], or by reaction of CH_3^+ (Table 1) or of CH_3O^4 [6d] with CH_3OCH_3 . Therefore, present results suggest that in interstellar clouds rich in CH_3OH and CH_3OCH_3 , the formation of $\text{CH}_3\text{OCH}_2^+$ and its reaction with NH_3 , and subsequent dissociative recombination can lead to CH_2NH , a known interstellar molecule. Similar reactions with alkylamines can lead to alkylimines.

Acknowledgement

We thank Dr. V. Anicich of JPL for making the ICR mass spectrometer available for the reported measurements.

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APPENDIX B

Reactions of $\text{CH}_3\text{OCH}_2^+$ with Hydrocarbons and O, N, and S Compounds: Applications for Chemical Ionization in Selected Ion Flow Tube Studies

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We report the results of a flowing afterglow ion source-selected ion flow tube study (FA-SIFT) of the reactions of the methoxymethyl cation, $\text{CH}_3\text{OCH}_2^+$. Rate coefficients and product branching ratios are reported for twenty nine reagent molecules including those that constitute the major ingredients of air, the hydrocarbons CH_4 , C_2H_6 , C_3H_8 , n- C_4H_{10} , C_2H_2 , C_2H_4 , C_3H_4 (allene and propyne), C_6H_6 , and the S-containing molecules H_2S , CH_3SH , $\text{C}_2\text{H}_5\text{SH}$, $(\text{CH}_3)_2\text{SH}$, and $(\text{C}_2\text{H}_5)_2\text{SH}$. In addition, we examined the reactions with the N-containing molecules NH_3 , CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$, pyrrole, pyridine as well as CH_3COCH_3 . The results can be summarized under three general reaction types: Reaction at the CH_3 carbon, reaction at the CH_2 carbon, and association. The results also indicate that the methoxymethyl cation can be used as a chemical ionization source for the detection of trace levels of S-containing compounds in saturated hydrocarbons. (J Am Soc Mass Spectrom 2002, 13, 1028–1033) © 2002 American Society for Mass Spectrometry

The technique of chemical ionization was first applied to analyte identification when ion-molecule chemistry was in its infancy [1–3]. In recent times there has been a renewal of interest in the technique as new methods that utilize chemical ionization have been developed. These new methods have been used for detecting trace volatile organic compounds (VOCs) in air. Commercially available instruments now offer chemical ionization sources as “electronic nose” type add-ons [4, 5]. Two recent methods that incorporate chemical ionization in combination with flow system methodology are *proton transfer mass spectrometry* as developed by Lindinger et al. [6] and *selected ion flow tube mass spectrometry* (SIFT-MS) developed by Smith and Spanel [7]. Most samples containing VOCs consist of only trace amounts of the VOCs in air. In order to detect those VOCs that may be present in concentrations as low as parts per billion (or even lower) by volume (ppb) in air, it is necessary that the chemical ionization precursor ion be “blind to” or unreactive with the bulk constituents of air (viz., N_2 , O_2 , CO_2 , Ar, H_2O). In the SIFT-MS technique, the precursor ions that are generally chosen for chemical ionization are themselves “terminal” ions derived from air itself:

They are H_3O^+ , O_2^+ , or NO^+ [7]. These ions are, of course, convenient to use as sources for chemical ionization as they are readily produced from an air discharge. A second requirement for a precursor ion for trace amounts of VOCs in air is that it must be easily produced from a discharge in large ion densities. Reactant ion signals are typically required to be in excess of 100,000 counts per s at the particle multiplier detector at the downstream mass spectrometer for VOC detection in the ppb or ppt range.

It has been found that the three ion precursors mentioned above, H_3O^+ , O_2^+ , and NO^+ , are not suitable for all gas mixtures. In this study we present data for the methoxymethyl cation, $\text{CH}_3\text{OCH}_2^+$, for consideration as a potential chemical ionization precursor for the detection of some VOCs in the presence of hydrocarbons.

The ion-molecule chemistry of $\text{CH}_3\text{OCH}_2^+$ has been investigated previously and reported in several studies in the literature. The experimental techniques that have been used include ion cyclotron resonance (ICR) and flow tube studies. These studies [8–15] are referred to in the Results and Discussion section of this paper. The reason for the considerable interest in the chemistry of $\text{CH}_3\text{OCH}_2^+$ is that it can react with reagents in two ways: Either at the CH_3 carbon or at the CH_2 carbon. Despite the considerable interest shown in the ion, the important reaction parameters such as the product

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channel ratios and rate coefficients have not been well characterized.

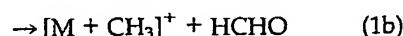
Experimental

The flowing afterglow ionization source combined with a selected ion flow drift tube (FA-SIFDT) used in our laboratory has been described previously [16]. In the present study, $\text{CH}_3\text{OCH}_2^+$ ions are generated mainly via Penning ionization from He (2^3S) metastables reacting with dimethoxymethane, $(\text{CH}_3\text{O})_2\text{CH}_2$. Small amounts of dimethoxymethane are added to a flowing helium afterglow produced via a microwave discharge. The $\text{CH}_3\text{OCH}_2^+$ ion formed in the flowing afterglow source is mass-selected and drifted into the reaction flow tube (operating pressure 0.48 torr) via a series of ion lenses that focus the ion swarm onto the entrance aperture of a venturi orifice [16]. Signals of $\text{CH}_3\text{OCH}_2^+$ in excess of 100,000 counts per second (cps) are readily achievable in our FA-SIFT instrument. A typical mass spectrum recorded by the downstream quadrupole mass filter after injection of $\text{CH}_3\text{OCH}_2^+$ is 55,000 cps of $\text{CH}_3\text{OCH}_2^+$ and two small peaks corresponding to CH_3^+ (<2000 cps) and C_2H_5^+ (<2000 cps). The two small peaks are the result of fragmentation of the primary ion during the injection process. As is usual with SIFT flow tube methodology, rate coefficients have an uncertainty of $\pm 15\%$.

Results and Discussion

Several isomeric structures of the ion $\text{C}_2\text{H}_5\text{O}^+$ are known to be stable in the gas phase including CH_3CHOH^+ (protonated acetaldehyde), $\text{CH}_2\text{CHOH}_2^+$ (protonated vinyl alcohol), $\text{CH}_2\text{OHCH}_2^+$ (protonated oxirane), and the ion that is the subject of this study, $\text{CH}_3\text{OCH}_2^+$. We have explored the different reactivities of these isomeric ions in an earlier study [17] which demonstrated that the ion injected here using the method described previously had the $\text{CH}_3\text{OCH}_2^+$ structure. We concentrate in this paper solely on the reactions of the methoxymethyl cation, $\text{CH}_3\text{OCH}_2^+$.

A number of earlier and mainly low pressure ion cyclotron resonance (ICR) investigations [8–15] have demonstrated that the methoxymethyl cation reacts with a nucleophile M in one of two ways:



At the higher pressures encountered within a flow tube, another product channel, that of association (eq 1c), may also be observed.



Although the gas phase chemistry of the methoxym-

ethyl cation has been well characterized in earlier ICR investigations [8, 10, 11, 13, 23], the key parameters (rate coefficients and product distributions) required for the application of $\text{CH}_3\text{OCH}_2^+$ as a chemical ionization agent in SIFT-MS are not well known. Indeed, the competition between bimolecular reaction and termolecular association (eq 1c) gives some insight into the stability of the ion-molecule complex. The greater reactant ion specificity of the flowing afterglow ion source used in this work [8] enables us to obtain more accurate product distributions than those reported in earlier studies. We report here accurate product distributions for flow tube studies for the first time.

We have summarised all the reactions investigated in this study in Table 1 and comment next on individual reactions.

Currently, the most comprehensive investigation of the reactivity of $\text{CH}_3\text{OCH}_2^+$ is the flowing afterglow study by Freitas and O'Hair [15]. They present arguments for a mechanism whereby $\text{CH}_3\text{OCH}_2^+$ acts as an ambident electrophile as it can react at the CH_3 carbon via an $\text{S}_{\text{N}}2$ methylation reaction (eq 1b) or at the CH_2 carbon via an addition-elimination reaction (eq 1a). However, there are some significant differences between the flowing afterglow experimental results [15] and those of the present study (see Table 1). There are no reasons inherent to either method why these differences should occur as both use similar operating flow tube pressures between 0.36 and 0.48 torr.

Freitas and O'Hair generated $\text{CH}_3\text{OCH}_2^+$ in their flowing afterglow by a two-step process. First they used electron impact on N_2O to generate NO^+ . Dimethyl ether was subsequently added downstream from the ionization region and resulted in formation of the methoxymethyl cation via the reaction



$$k = 8.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

The rate coefficient represents the total disappearance of NO^+ and the numbers above each arrow refer to the measured branching ratios.

Our measured parameters for reaction (eq 2) are in good agreement with the results of Freitas and O'Hair who reported a rate coefficient of $7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ [15].

In an attempt to resolve the differences in results between the measurements of Freitas and O'Hair [15] and this work, we examined several reactions of N_2O^+ , which was also present in their flowing afterglow experiment. These included

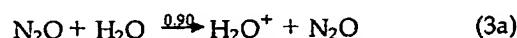


Table 1. Reaction rate coefficients and product ratios for the reactions of $\text{CH}_3\text{OCH}_2^+$ with the given reagent (numbers in parenthesis are previous measurements that have their origin indicated in the Table footnotes)

Reagent	k_{obs}^a	k_{coll}^b	$[\text{M} + \text{CH}]^+$	$[\text{M} + \text{CH}_3]^+$	$[\text{M} + \text{CH}_3\text{OCH}_2]^+$	Other
O ₂	<0.0005	0.68	nr ^c			
N ₂	<0.0005	0.74	nr			
CO	<0.0005	0.82	nr			
CO ₂	<0.0005	0.81	nr			
Ar	<0.0005	0.66	nr			
N ₂ O	<0.0005	0.90	nr			
H ₂ O	<0.0005 (0.01) ^d	2.50	nr		nr(1.0) ^d	
CH ₄	<0.0005	1.1	nr			
C ₂ H ₆	<0.0005	1.2	nr			
C ₃ H ₈	<0.0005	1.3	nr			
n-C ₄ H ₁₀	<0.0005	1.3	nr			
C ₂ H ₂	<0.0005	1.1	nr			
C ₂ H ₄	<0.0005	1.2	nr			
CH ₃ C≡CH	0.81	1.3	0.20	0.40	0.40	
CH ₂ CCH ₂	0.37	1.3	0.10	0.70	0.20	
C ₆ H ₆	0.49 (1.9) ^d (0.5) ^e	1.4	1.0 (0.85) ^d (1.0) ^e		(0.15) ^d	
NH ₃	0.65 (0.4) ^d (0.59) ^f (2.3) ^g (0.43) ^h	2.3	0.95 (0.70) ^d (1.0) ^f (0.58) ^g	0.05 (0.10) ^d (0.16) ^g	0.0 (0.2) ^d	(0.26) ^g
ND ₃	0.60	2.2	0.80	0.20		
CH ₃ NH ₂	1.1 (1.6) ^d (1.50) ^g (0.94) ^h	1.9	0.95 (0.05) ^d	0.05 (0.25) ^d	0.0 (0.70) ^d	
(CH ₃) ₂ NH	0.94 (1.2) ^d (0.37) ^e	1.6	0.70 (0.65) ^d	0.0 (0.05) ^d	0.3 (0.3) ^d	
(CH ₃) ₃ N	1.30 (2.3) ^d (1.40) ^g	1.5	0.0	0.0 (0.05) ^d	0.70 (0.95) ^d	0.30 ⁱ
C ₄ H ₅ N (pyrrole)	2.0	2.1	0.45	0.0	0.55	
C ₅ H ₅ N (pyridine)	2.20 (1.5) ^d	2.5	0.0 (0.15) ^d	0.05 (0.15) ^d	0.95 (0.70) ^d	
CH ₃ COCH ₃	0.76 (1.8) ^d	3.0		0.2 (0.1) ^d	0.80 (0.9) ^d	
H ₂ S	<0.0005 (3.0) ^d	1.3	nr (0.9) ^d	nr (0.05) ^d	nr (0.05) ^d	
CH ₃ SH	0.31 (0.6) ^d	1.9	0.05 (0.65) ^d	0.0 (0.05) ^d	0.95 (0.30) ^d	
C ₂ H ₅ SH	0.90 (1.0) ^d	2.0	0.85 (0.30) ^d	0.0 (0.25) ^d	0.15 (0.45) ^d	
(CH ₃) ₂ S	1.4 (2.3) ^d	2.0	0.0 (0.0) ^d	0.05 (0.05) ^d (1.0) ^j	0.95 (0.95) ^d	
(C ₂ H ₅) ₂ S	1.90	2.0			1.0	

^aObserved rate coefficient in units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

^bCalculated collision rate as described in reference [18] in units of $10^{-9} \text{ cm}^3 \text{ s}^{-1}$.

^cNo reaction observed.

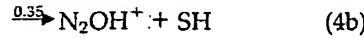
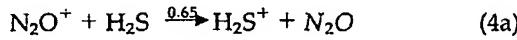
^dReference [15] ^eReference [17] ^fReference [14] (SIFT)

^gReference [19]

^hReference [14] (ICR) ⁱThe other product is $(\text{CH}_3)_2\text{NCH}_2^+ + \text{CH}_3\text{OCH}_3$

^jReference [11], low pressure ICR study.

$$k = 2.1 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



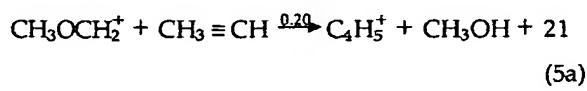
$$k = 1.30 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$

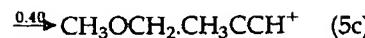
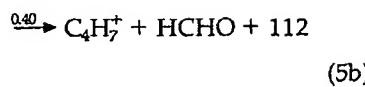
Water, at trace levels, is always present in the flow tube and therefore some N_2OH^+ ions will be formed through reaction (eq 3b). It is unfortunate that N_2OH^+ is isobaric with $\text{CH}_3\text{OCH}_2^+$ and its presence in the flow tube experiments of Freitas and O'Hair will thus influence both the observed rate coefficients and the product distributions. A similar situation occurs with H₂S where the extent of N_2OH^+ formation is even greater than with H₂O. We note that quite different results were found in our work for reactions of $\text{CH}_3\text{OCH}_2^+$ with these reagents (H₂O and H₂S) compared to those of Freitas and O'Hair. Differences in the results for other

reactions can be attributed to difficulties inherent to the flowing afterglow technique arising from the presence of multiple reactant ions. Freitas and O'Hair give error limits to their branching ratios of $\pm 50\%$, whereas in the selected ion flow tube the error limits are typically $\pm 10\%$ [8].

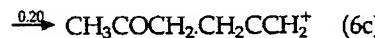
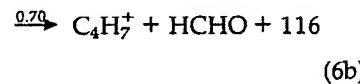
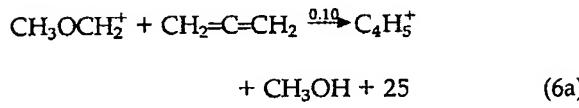
Reactions of $\text{CH}_3\text{OCH}_2^+$ with Hydrocarbons

No reactions were observed with any of the alkanes studied in this work (CH_4 , C_2H_6 , C_3H_8 , n-C₄H₁₀) as well as ethene and ethyne, ($k < 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$). Reactions were found to occur for propyne, allene and benzene (reaction exothermicities are indicated with the products in kJ mol^{-1} based on a value for $\Delta_f\text{H}^\circ [\text{CH}_3\text{OCH}_2^+]$ = 662 kJ mol^{-1} [9]):

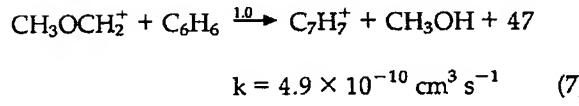




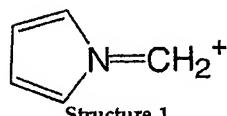
$$k = 8.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$



$$k = 3.7 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}.$$

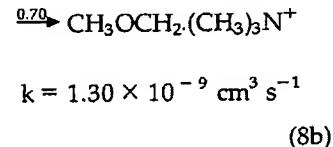
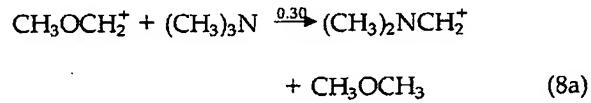


$$k = 4.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$



Structure 1

discussed previously by Pau et al. [10], Okada et al. [22], Caserio and Kim [23], and more recently by Freitas and O'Hair [15]. Initial attack of the $-\text{CH}_2^+$ carbon at N followed by elimination of CH_3OH . Adduct formation is the main product channel observed for trimethylamine and also for the cyclic amines pyrrole and pyridine. The reaction with trimethylamine yields an additional product channel (eq 8a) that is unique within the range of reactant molecules studied.



The reactions with propyne and allene are interesting in that the rate coefficients and product distributions for the isomers are quite different: More so than for most other ion-molecule reactions of these isomers [20]. The reaction of $\text{CH}_3\text{OCH}_2^+$ with propyne is more than twice as fast as the reaction with allene and it is the association channel that is responsible for much of the difference. These results are consistent with the loss of CH_3OH and HCHO from the reactions of $\text{CH}_3\text{OCH}_2^+$ with the hydrocarbons propene and but-2-ene that was observed in ICR studies [13].

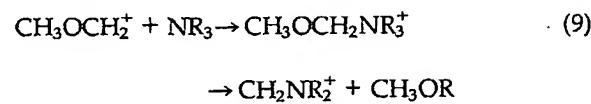
The results for benzene are in excellent agreement with our earlier measurement of this reaction [9], but differ from the results reported by Freitas and O'Hair for the reasons discussed earlier. The reaction has a single channel with an addition-elimination mechanism after electrophilic attack on benzene by the $-\text{CH}_2^+$ carbon, followed by CH_3OH loss. The C_7H_7^+ product ion is likely to have the benzyl structure as the amount of energy available is less than is necessary to cross the isomerization barrier of $301.5 \text{ kJ mol}^{-1}$ leading to the tropylium structure [21]. There is also insufficient energy within the complex to allow rearrangement to the tropylium structure.

Reactions of $\text{CH}_3\text{OCH}_2^+$ with N-Containing Compounds

The reactions with amines and other molecules containing a nitrogen atom were all fast and all exhibited the addition-elimination reaction yielding $(\text{M} + \text{CH})^+ + \text{CH}_3\text{OH}$ as the major reaction channel.

The general mechanism for these reactions has been

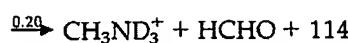
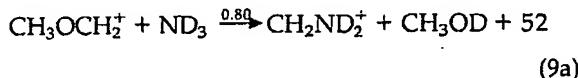
Although the neutral product is CH_3OCH_3 and not CH_3OH from the addition/elimination reaction, the mechanism is the same. In this case, however, a CH_3 group is transferred from trimethylamine to the O centre of $\text{CH}_3\text{OCH}_2^+$ and not a proton as is the case with primary and secondary amines. In all cases the addition-elimination proceeds by the mechanism:



Where one of the R groups is H, this is transferred to the CH_3O leaving group in preference to CH_3 transfer which may have a higher energy barrier. However, with $(\text{CH}_3)_3\text{N}$ the H transfer channel is not available and CH_3 is transferred. The leaving group is likely to be CH_3OCH_3 instead of CH_3OH . The product ions are likely in all cases to be the N-alkylated imines $(\text{R}_2\text{N}=\text{CH}_2)^+$. These ions have no unprotonated neutral conjugated bases, but rather can be viewed as alkylation products of the N-alkylated imines $(\text{H}_2\text{C}=\text{NR})\text{R}^+$. It is interesting to note that addition-elimination also occurs with c-C₄H₅N (pyrrole) which behaves in a manner that is similar to the primary amines. The elimination step for pyrrole probably involves the nitrogen-bound hydrogen, C₄H₄N-H, and the resulting product is possibly the protonated cyclic imine, Structure 1, (c-C₄H₄N=CH₂)⁺. On the other hand, in pyridine, where no N-H hydrogen is available, addition-elimination is not observed.

The reaction with ammonia has been discussed in

some detail by Okada et al. [22]. In an experiment with ND₃, the distribution of D that we observed among the product ions is given by



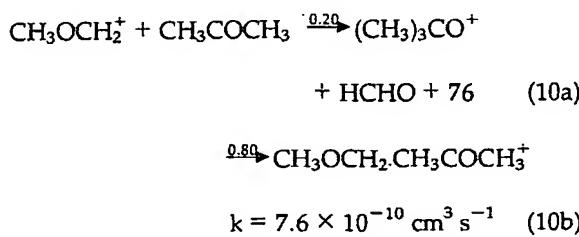
$$k = 6.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (9b)$$

that is consistent with the addition-elimination mechanism for (eq 9a) and an S_N2 mechanism for (eq 9b) as discussed in earlier investigations [17, 22].

Our observed rate coefficient and product distributions differ from those of Freitas and O'Hair [15], as discussed previously, but are consistent with earlier measurements from our laboratory [17].

Reactions of CH₃OCH₂⁺ with O- and S-Containing Compounds

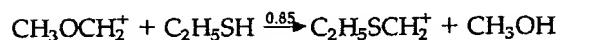
The molecules examined in reaction with CH₃OCH₂⁺ were CH₃COCH₃, H₂S, CH₃SH, C₂H₅SH, (CH₃)₂S, and (C₂H₅)₂S. For all reagents except H₂S ($k < 5 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$), reactions were observed and the association channel was a major outcome of reaction in most cases. Freitas and O'Hair note that whereas amines undergo addition-elimination reactions, most molecules containing O nucleophiles undergo methylation [15]. The reaction with acetone has been examined in several earlier low pressure ICR studies [11–13] in which the methyl transfer reaction was observed. Under low pressure ICR conditions ($< 10^{-5}$ torr) no adduct formation (eq 10b) was reported indicating that the metastable adduct ion lifetime is too short for collisional stabilization to be fast in the ICR. However, at the higher pressures of flow tubes, collisional stabilization is a major outcome of reaction as shown in reaction (eq 10).



The reactions of CH₃OCH₂⁺ with the thiols CH₃SH and C₂H₅SH, exhibit an addition-elimination mechanism, giving (M + CH)⁺ + CH₃OH, occurring in competition with adduct formation but in both cases the rate coefficient is substantially less than the collision rate coefficient (see Table 1).



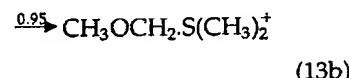
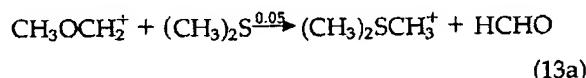
$$k = 3.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (11b)$$



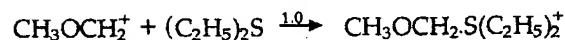
$$k = 9.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad (12b)$$

As the channel competing with adduct formation for both thiols is the addition-elimination reaction, it might be expected that the adduct ion structure has the form RSH₂OCH₃⁺ or, more likely, RSHCH₂OCH₃⁺ with the sulfur site of higher proton affinity being protonated [15].

On the other hand, the reactions with the sulfides (CH₃)₂S and (C₂H₅)₂S seemed to favor S_N2 substitution although, in both cases, adduct formation was the dominant channel.



$$k = 1.4 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$$



$$k = 1.9 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1} \quad (14)$$

If the S_N2 mechanism is in fact operating in these two reactions, as is indicated by the products with dimethyl sulfide observed in (eq 13a) and in the low pressure ICR study of Kim and co-workers [10], then the adduct ion structure is likely to be MCH₃OCH₂⁺ where M = (CH₃)₂S or (C₂H₅)₂S. The fact that both reactions occur at rates close to the collision rate (see Table 1), implies that the collision complex lifetime is sufficiently long for collision stabilization to be effective for all (or almost all) complexes.

Conclusion

The methoxymethyl cation CH₃OCH₂⁺ can be injected into a flow tube from a flowing afterglow ion source in sufficient number density to produce an effective source for chemical ionization. The non-reaction of CH₃OCH₂⁺ with saturated hydrocarbons and its fast

reaction with molecules containing sulfur provides an efficient way of quantifying thiols (mercaptans) and sulfides in hydrocarbons, whether present naturally or added as odorants. The data provided here enables the absolute detection of sulfur-containing molecules in mixtures of hydrocarbons down to 20 parts per billion using SIFT-MS methodology.

A final comment concerns the ease of adduct formation observed in many reactions of $\text{CH}_3\text{OCH}_2^+$ at flow tube pressures. Association adducts were produced efficiently at pressures of 0.48 (M = He) in reactions of some amines, ketones, thiols, and sulfides. That many of these adducts were formed at or near the collision rate indicates that the ion-molecule collision complexes are sufficiently long-lived ($\tau \gg 0.03 \mu\text{s}$) to be stabilized by collision with the bath gas before extensive fragmentation can occur. In some reactions almost every complex formed is stabilized by collision and fragmentation does not occur to any significant extent. The adducts formed in these circumstances are strongly-bound covalent ions whose structures may be of the type $\text{MCH}_2\text{OHCH}_3^+$ (M = nucleophile – H) if an addition-elimination mechanism dominates, or $\text{MCH}_3\text{OCH}_2^+$ (M = nucleophile), when an $\text{S}_{\text{N}}2$ mechanism dominates.

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